NEW APPLICATION OF SANS: STUDYING ADSORPTION OF SUPERCRITICAL FLUIDS IN NANOPORES

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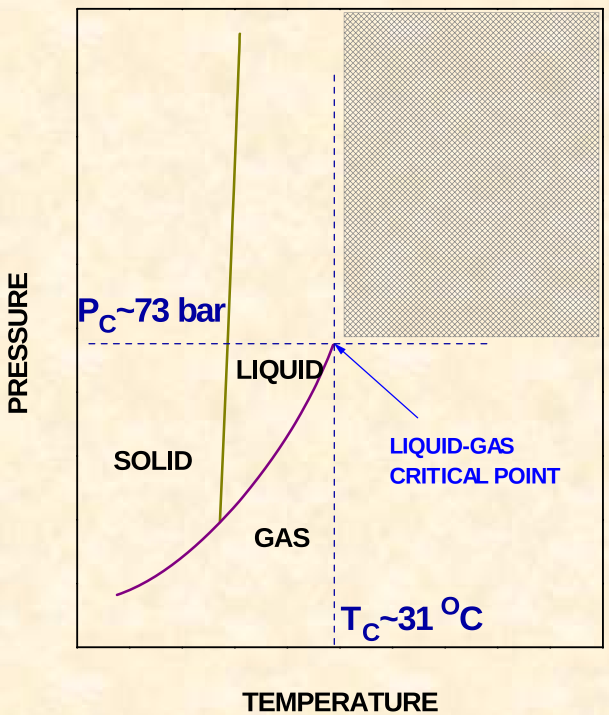
MOTIVATION

SUPERCRITICAL FLUID IS A SUBSTANCE AT (T) AND (P) ABOVE THE GAS-LIQUID CRITICAL POINT

TUNABLE SOLVENT POWER AND ADVANTAGEOUS MASS TRANSFER PROPERTIES MAKE SCF AN ATTRACTIVE ALTERNATIVE TO LIQUID SOLVENTS

- **HETEROGENEOUS CATALYSIS**
- **ADSORPTIVE SEPARATIONS**
- **REGENERATION OF ADSORBERS**
- **SCF CHROMATOGRAPHY**



GENERIC PHASE DIAGRAM OF CARBON DIOXIDE

ADSORPTION IN POROUS MEDIA IS TRADITIONALLY MEASURED BY GRAVIMETRIC, VOLUMETRIC, TOTAL DESORPTION AND SIMILAR METHODS

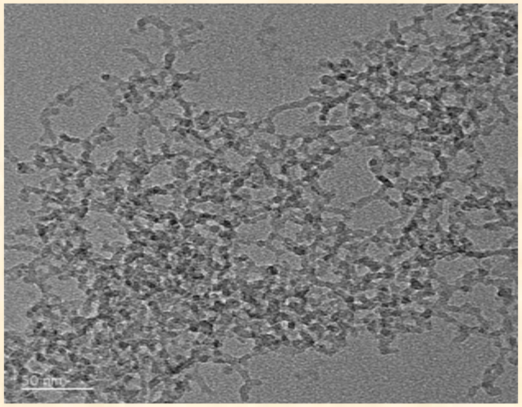
SANS HAS BEEN USUALLY APPLIED TO STUDY GASES AND LIQUIDS IN SMALL PORES:

- **STRUCTURE OF MULTICOMPONENT POROUS SYSTEMS VIA CONTRAST MATCHING ONE OF THE PHASES WITH H+D LIQUIDS**

- **STRUCTURE OF PORES BY VIA GRADUAL SATURATION OF PORES WITH CONTRAST MATCHING MIXTURE OF H+D GASES**

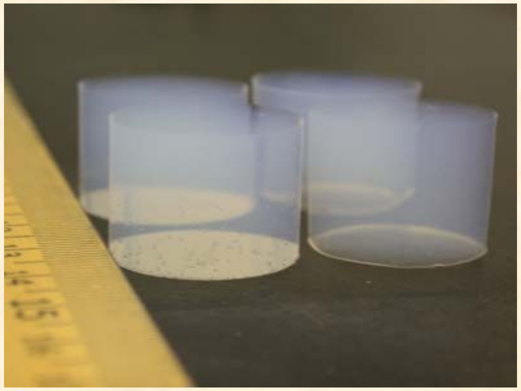
SANS STUDY OF THE ADSORPTION OF A SUPERCRITICAL FLUID IN NANOPORES

POROUS SYSTEM: AEROGEL



AEROGELS ARE VERY DILUTE NETWORKS
OF RANDOMLY INTERCONNECTED SiO_2 STRANDS

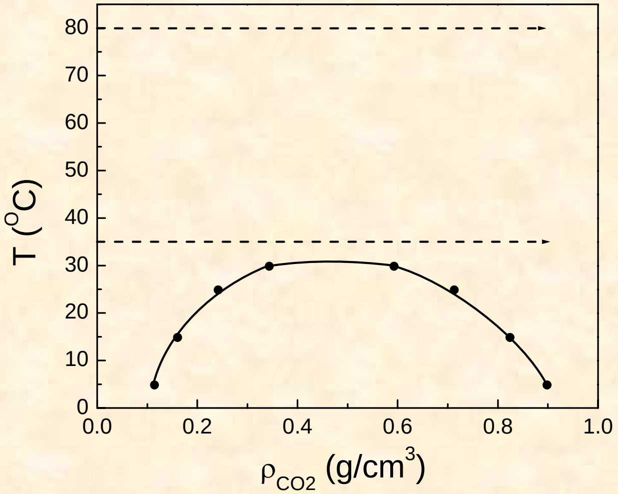
BASE CATALYZED AEROGELS FROM OCELLUS
Inc. WITH ρ_{SiO2} = 0.1 g/cc



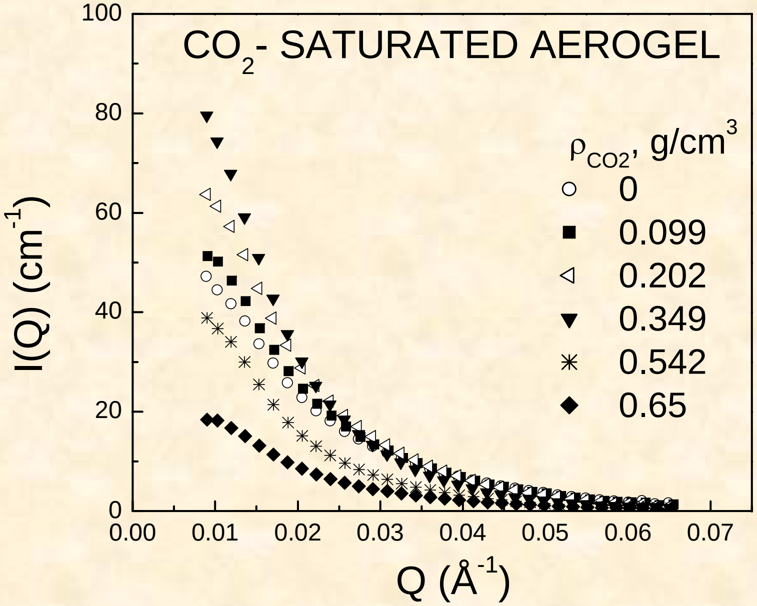
PORE VOLUME V_p ~ 96 %
PORE DIAMETER ~ 70 Å
SURFACE AREA S/V ~ 400 m^2/g
SURFACE METOXY GROUPS =Si-O-CH_3

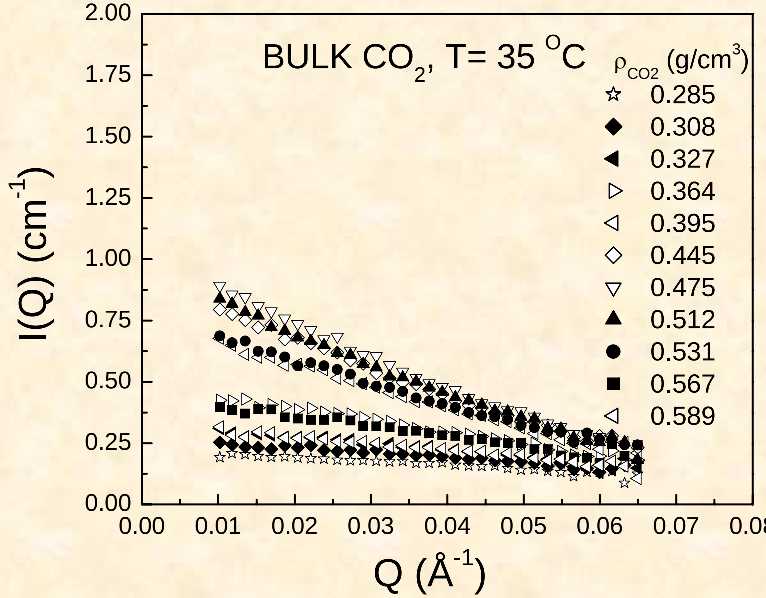
SCF: CO_2, T_C=31.1 ^OC, ρ_C = 0.468 g/cc

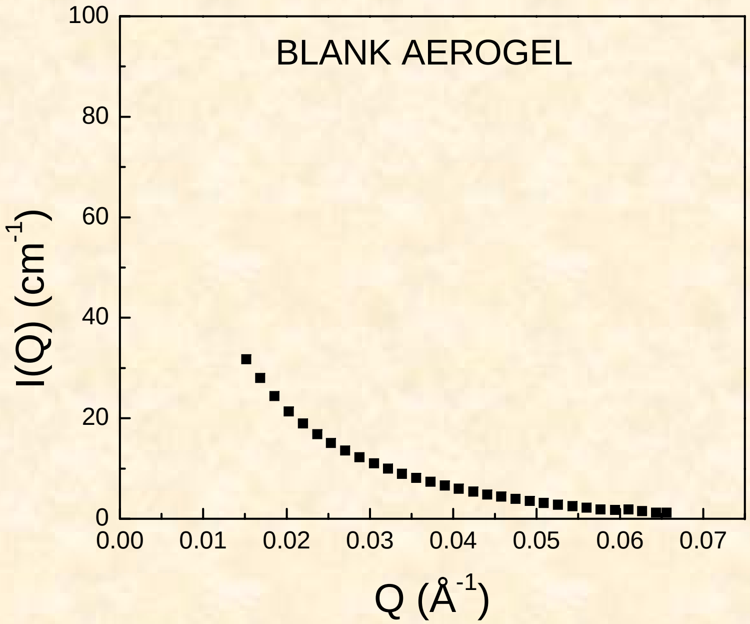
P-SCANS AT T=35 AND 80 ^OC



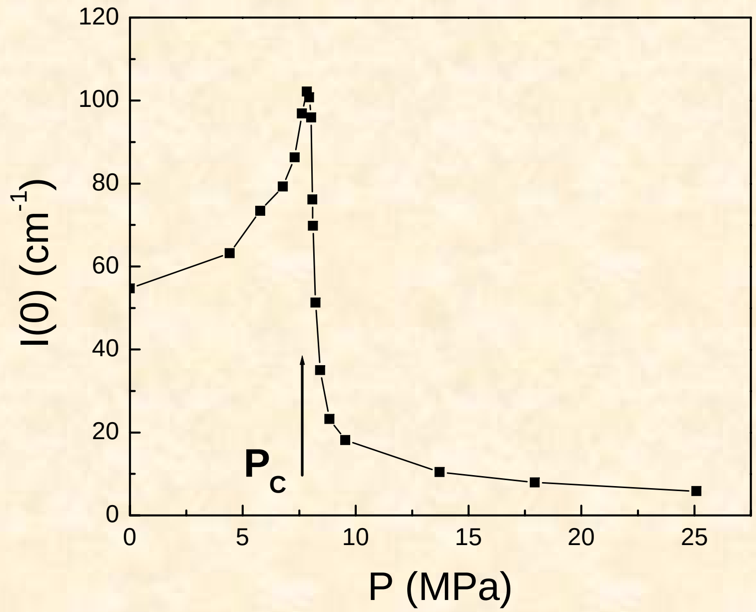
SANS FROM CO_2-SATURATED AEROGEL AT T=35 ^{O}C





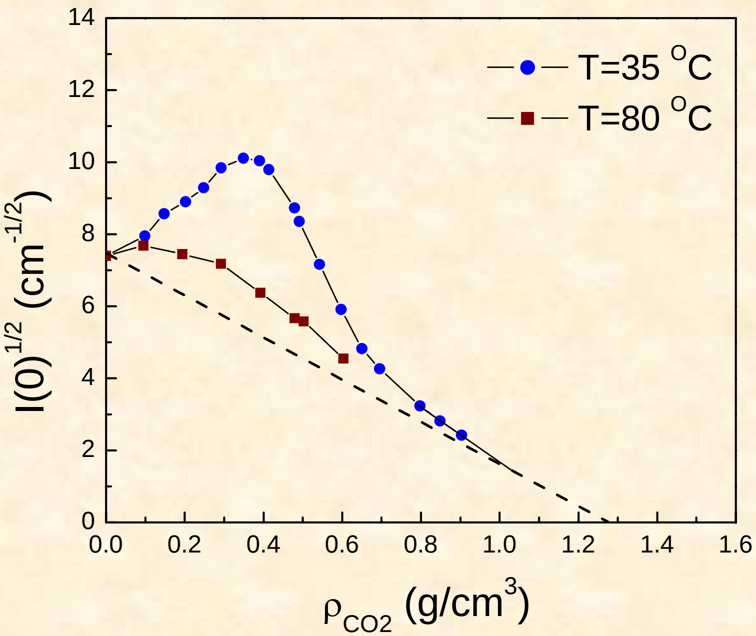


THE VARIATION OF SCATTERING WITH DENSITY/PRESSURE IS NON-MONOTONIC. IT EXCEEDS SCATTERING FROM BULK CO_2 BY TWO ORDERS OF MAGNITUDE AND THAT FROM BLANK AEROGEL BY A FACTOR OF THREE.

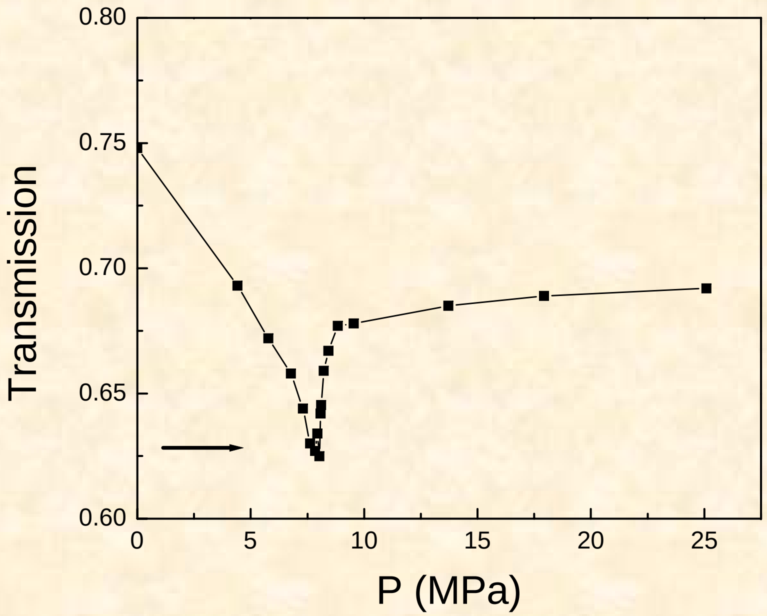


SANS FROM A TWO-PHASE SYSTEM (CO_2+AEROGEL):

$$I(0) \sim \left(\rho_1^* - \rho_2^*\right)^2 = \left(\frac{b_{SiO2}}{M_{SiO2}}\rho_{SiO2} - \frac{b_{CO2}}{M_{CO2}}\rho_{CO2}\right)^2$$



DEVIATION FROM THE STRAIGHT LINE $I(0)^{1/2} \sim \rho_{CO2}$ INDICATES FORMATION OF A THIRD (ADSORBED) PHASE

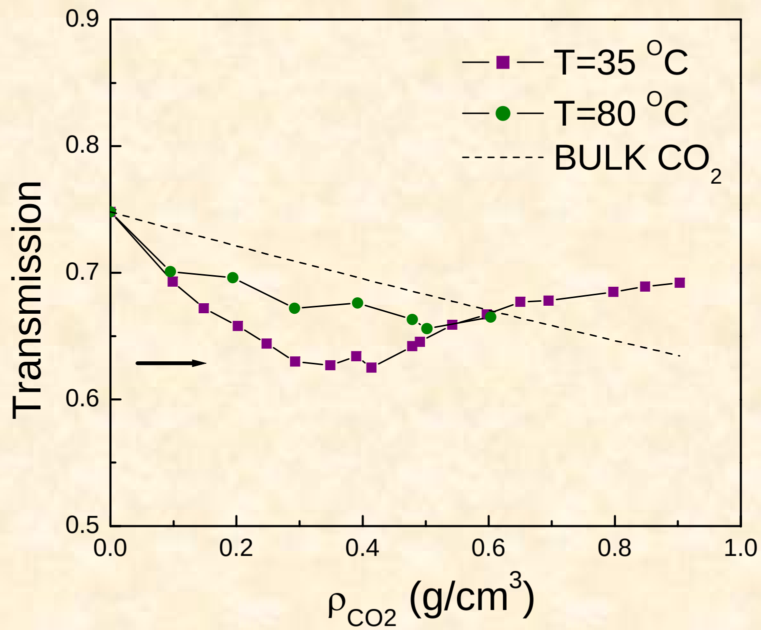


NEUTRON TRANSMISSION $T = \frac{I_{transm}}{I_{inc}}$

TRANSMISSION OF A TWO-PHASE SYSTEM (CO_2+ AEROGEL):

$$T_2 = \exp(-N_{SiO2}\sigma_{SiO2}t - N_{CO2}\sigma_{CO2}t) =$$

$$= T_1 \exp(-N_{CO2}\sigma_{CO2}t) = T_2 = T_1 \exp(-C\rho_{CO2}t)$$



DEVIATION FROM THE DASHED LINE $\ln T_2 \sim \rho_{CO2}$ CONFIRMS FORMATION OF A THIRD (ADSORBED) PHASE

DETERMINATION OF EXCESS ADSORPTION

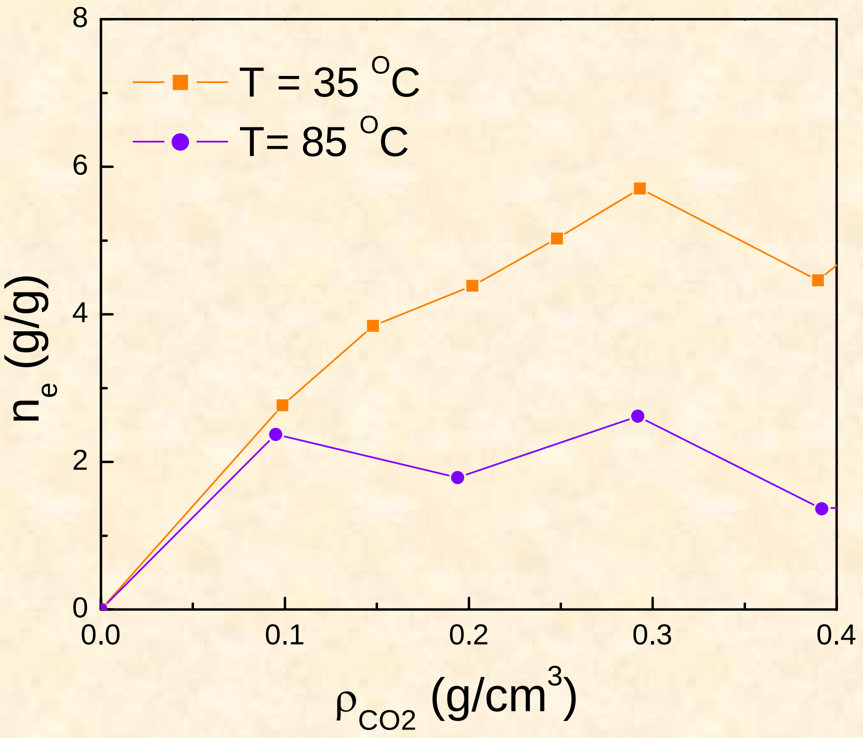
EXCESS OR GIBBS ADSORPTION (n_e) IS PARAMETER CALCULATED NEGLECTING THE VOLUME OCCUPIED BY THE ADSORBED PHASE, I.E. AS IF THE ENTIRE PORE VOLUME WAS ACCESSIBLE TO UNADSORBED FLUID

"EXCESS" NUMBER DENSITY OF ADSORBED MOLECULES

$$N_e = \frac{\ln T_2 - \ln T_3}{\sigma_{CO2} t}$$

"EXCESS" ADSORPTION PER GRAM OF ADSORBENT

$$n_e = \frac{M_{CO2} N_e}{\rho_{aerogel} N_{Av}}$$



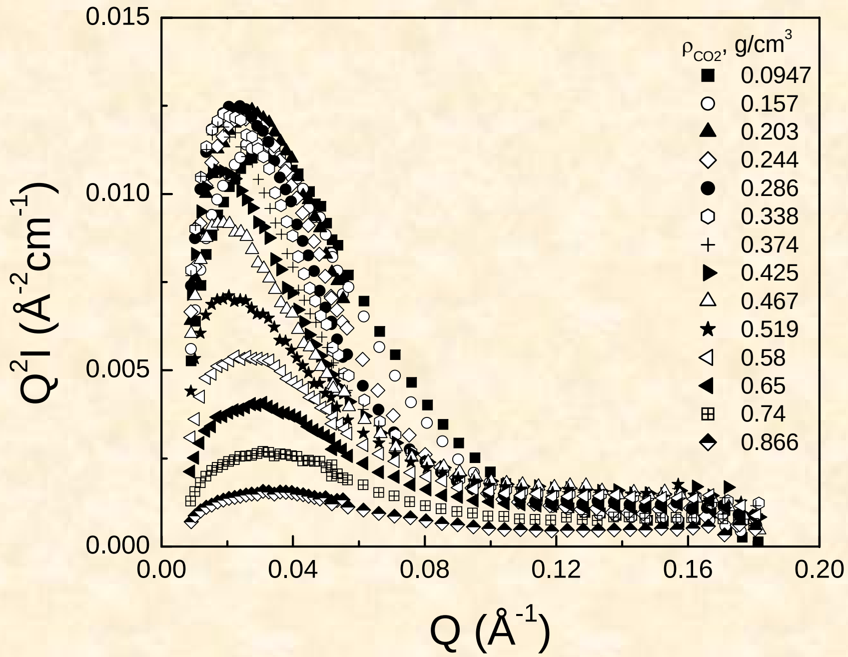
DETERMINATION OF VOLUME FRACTION

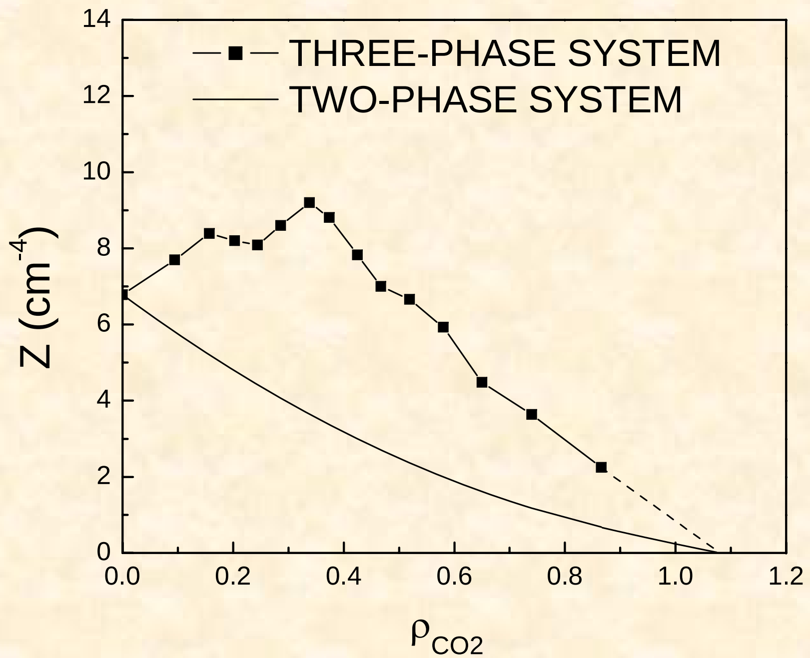
THE INVARIANT FOR A TWO-PHASE SYSTEM (AEROGEL+CO_2)

$$Z_0(\rho_{CO2}) = \int_0^\infty Q^2 I_0(Q,\rho_{CO2})dQ = 2\pi^2\phi_1(1-\phi_1)(\rho_1^* - \rho_2^*)^2$$

THE INVARIANT FOR A THREE-PHASE SYSTEM (Wu, Polymer, 1982)

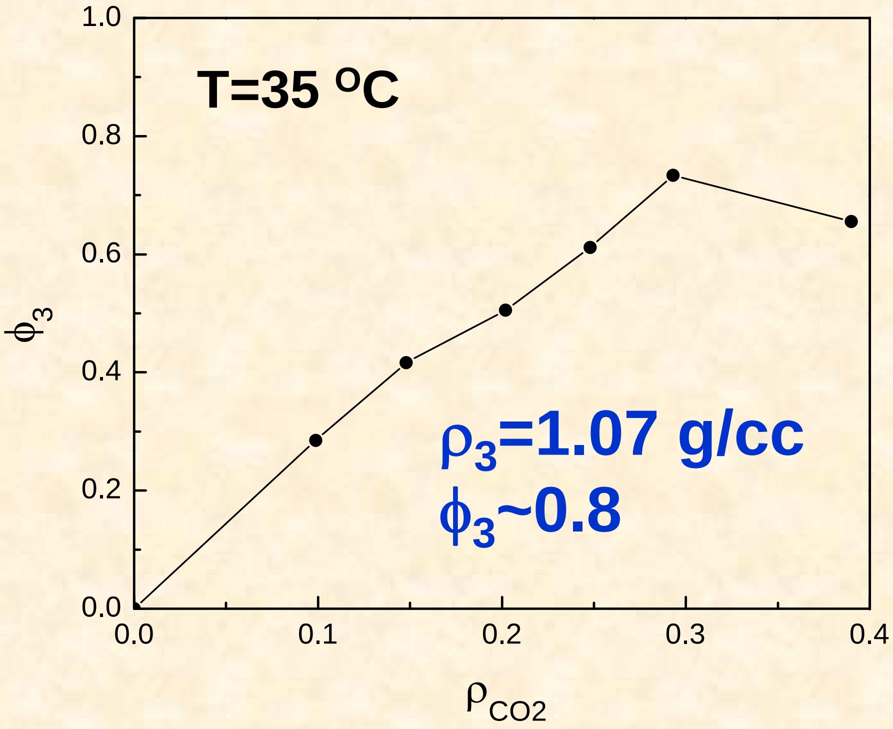
$$Z(\rho_{CO2}) = \int_0^\infty Q^2 I(Q,\rho_{CO2})dQ =$$
$$= 2\pi^2\left[\phi_1\phi_2(\rho_1^* - \rho_2^*)^2 + \phi_2\phi_3(\rho_2^* - \rho_3^*)^2 + \phi_1\phi_3(\rho_1^* - \rho_3^*)^2\right]$$





THE VOLUME FRACTION OF THE ADSORBED PHASE CAN BE CALCULATED FROM THE DIFFERENCE OF INVARIANTS:

$$\phi_3 = \frac{Z - Z_0}{2\pi^2\left[\phi_2(\rho_2^* - \rho_3^*)^2 + \phi_1(\rho_1^* - \rho_3^*)^2 - \phi_1(\rho_1^* - \rho_2^*)^2\right]}$$



CONCLUSIONS

- **SANS COMBINED WITH THE TRANSMISSION MEASUREMENTS CAN BE USED TO STUDY THE ADSORPTION OF SCFs IN POROUS MATERIALS**

- **AT ($T \sim T_C$, $P \sim P_C$) AN EXTREMELY COMPRESSED ADSORBED PHASE IS FORMED WITH THE DENSITY ~ 1.1 g/cc SIMILAR TO CLOSELY PACKED CO_2 MOLECULES WITH THE vdW VOLUME**

- **IN THE MAXIMAL ADSORPTION REGIME n_e=5.74 g/g TO BE COMPARED WITH n_e~0.2 IN ZEOLITES and n_e~0.9 IN SUPERACTIVATED CARBON**

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